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(54) POWDER COATING COMPOSITIONS

(71) We, FORD MOTOR COMPANY LIMITED, a British Company of Eagle Way, Basildon, Essex, CM13 3BW, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to powder coating compositions.

Powder coating compositions are extremely desirable for use in painting substrates in that they are essentially free of the organic solvents conventionally utilized in liquid paint systems. Thus, they give off little, if any, volatile material to the environment when heat cured.

Powder coatings comprising (1) a copolymer of a glycidyl acrylate and other olefinically unsaturated monomers, (2) a crosslinking agent comprising a dicarboxylic acid, a mixture of dicarboxylic acid and a monocarboxylic acid or a carboxy terminated polymer and (3) a polymeric flow control agent are described in Patent Specification No. 1,334,354.

Powder coating materials comprising (1) a copolymer of a hydroxy acrylate and other olefinically unsaturated monomers, (2) a crosslinking agent selected from anhydrides, dicarboxylic acids, and melamines, and (3) a polymeric flow control agent are described in Patent Specification No. 1,340,154.

It now has been discovered that powder coating compositions having unexpected advantages relative to the afore-described compositions can be obtained merely by modifying the copolymer so that it has both hydroxy-functionality and epoxy-functionality provided by the glycidyl acrylate. This is accomplished by including from 2 to 10 weight percent of a C₅—C₇ hydroxyalkyl acrylate and from 5 to 20 weight percent of a glycidyl ester of a monoethylenically unsaturated carboxylic acid, e.g. glycidyl acrylate and glycidyl methacrylate, with the

olefinically unsaturated monomers which make up the rest of the copolymer.

According to the invention, therefore, there is provided a powder coating composition comprising a mixture of:

- (A) A copolymer derived from 5 to 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid, from 2 to 10 percent by weight of a C₅—C₇ hydroxyalkyl acrylate or methacrylate and from 70 to 93 percent by weight of one or more other monoethylenically unsaturated monomers, and having a glass transition temperature of from 40 to 90°C and a number average molecular weight of from 1500 to 15,000, and
(B) a saturated, straight chain, aliphatic dicarboxylic acid containing from 4 to 20 carbon atoms present in an amount to provide from 0.8 to 1.1 carboxyl groups for each functional group (i.e. epoxy or hydroxy group) in the copolymer.

Except in those instances wherein a specific compound is named, the term "acrylate" is used in this specification to include esters of both acrylic acid and methacrylic acid, i.e. both acrylates and methacrylates. The powders prepared in accordance with this invention are more compatible. They are easily and more effectively processed by spray drying in that they resist phase separation. They may also be processed by melt blending and vacuum drying techniques. They are easily and effectively mixed by extrusion or mill rolling. Further, the need for an anti-static agent is eliminated when a film depth of less than 4 mils (0.004 in.) is to be applied.

Epoxy and hydroxy functional copolymers suitable for use in the powder coating materials of this invention are readily formed by conventional free radical induced polymerization of suitable alpha-beta olefinically

unsaturated monomers. These copolymers having both pendant epoxide groups and pendant hydroxyl groups are potentially self-crosslinking but the epoxy-hydroxy reaction is very slow and requires large amounts of catalyst to accelerate the curing reaction. Thus, in this invention, a crosslinking agent, i.e. a dicarboxylic acid, is added to the paint binder system.

The copolymers used in this invention contain from 5 to 20, preferably from 8 to 15, weight percent of a glycidyl ester of a monoethylenically unsaturated carboxylic acid, e.g. glycidyl acrylate or glycidyl methacrylate. These monomers provide the copolymer with its epoxy functionality. The hydroxy functionality is provided by incorporating in the unsaturated monomer polymerization mix from 2 to 10 weight percent of a hydroxy acrylate. The hydroxy acrylate is preferably an ester of a C_2-C_6 dihydric alcohol and acrylic or methacrylic acid. Of these 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate are the most preferred.

The remainder of the copolymer consists essentially of one or more monofunctional, alpha-beta olefinically unsaturated monomers. These can be acrylates or a mixture of acrylates and monovinyl hydrocarbons. Preferably, in excess of fifty weight percent of the copolymer monomers are esters of a C_1-C_6 monohydric alcohol and acrylic or methacrylic acid, e.g. methyl methacrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, hexyl acrylate or 2-ethylhexyl methacrylate. C_6-C_{10} monovinyl hydrocarbons, such as styrene, alpha-methyl styrene, vinyltoluene, t-butylstyrene, and chlorostyrene, are suitable for use but preferably comprise less than fifty weight percent of the copolymer. Other vinyl monomers such as vinyl chloride, acrylonitrile, methacrylonitrile, and vinyl acetate may be used as modifying monomers. When employed these comprise between 0 and 30 percent by weight of the monomer mixture.

The epoxy-functional and hydroxy-functional copolymers used in these coating compositions have a glass transition temperature of from 40°C. to 90°C., preferably from 50°C. to 80°C., and a molecular weight

(\bar{M}_n) of from 1500 to 15,000, preferably from 2500 to 6,000.

In preparing this copolymer, the epoxy-functional monomer, e.g. glycidyl methacrylate, and the hydroxy-functional monomer, e.g. 2-hydroxyethyl methacrylate, are mixed with the other ethylenically unsaturated monomer(s) and reacted by conventional free radical initiated polymerization in such proportions as to obtain the copolymer for the powder coating compositions. Thus, when the preferred ethylenically unsaturated re-

mainder monomers are used with the epoxy-functional monomer to form the copolymer, the epoxy-functional monomer is present in the copolymer in an amount of from 5 weight percent to 20 weight percent, the hydroxy-functional monomer is present in the copolymer in an amount of from 2 to 10 weight percent, and the preferred other monomers are present in an amount of from 93 to 70 weight percent. Generally, a free radical initiator is needed to induce the polymerization reaction. A large number of free radical initiators are known to the art and are suitable for this purpose. These include benzoyl peroxide, lauryl peroxide, t-butylhydroperoxide, acetylcyclohexane sulfonyl peroxide, diisobutyl peroxide, di-(2-ethylhexyl) peroxydicarbonate, diisopropyl peroxydicarbonate, t-butyl-peroxyisovalate and decanoyl peroxide, azobis (2-methylpropanitrile). The polymerization is preferably carried out in solution using a solvent in which the epoxy-functional, hydroxy-functional copolymer is soluble. Toluene, xylene, dioxane and butanone are suitable solvents for this polymerization. If the epoxy-functional, hydroxy-functional copolymer is prepared in solution, the solid copolymer can be precipitated by pouring the solution at a slow rate into a non-solvent for such copolymer, such as hexane, octane or water, under suitable agitation. The copolymer thus obtained is further dried so that it contains less than three percent of the materials that volatilize at the temperatures used for baking the coatings.

These copolymers can also be prepared by emulsion polymerization, suspension polymerization, bulk polymerization or their suitable combinations. In these methods of preparing the copolymers, chain transfer agents may be required to control the molecular weight of the copolymer to a desired range. The solid copolymers obtained by these methods must also be dried to contain less than three percent of the materials that volatilize at the temperatures used for baking the coatings.

For powder coating applications, both the molecular weight and molecular weight distribution of the epoxy-functional, hydroxy-functional copolymer are important. While

the molecular weight (\bar{M}_n) range extends from 1500 to 15,000, the copolymer component must not contain significant amounts of higher molecular weight fractions. No more than 5 percent of the copolymer should be of a molecular weight greater than 20,000. The molecular weight distribution as measured by the ratio of weight average molecular weight to number average mole-

cular weight (\bar{M}_w/\bar{M}_n) should be from 1.6

to 3.0. The preferred range of molecular weight distribution is from 1.7 to 2.2.

These powder coating compositions include as crosslinking agents for the copolymers saturated, straight chain, aliphatic, dicarboxylic acid containing 4 to 20 carbon atoms per molecule in an amount of from 0.8 to 1.1 carboxyl groups for each functional group (i.e. epoxy groups and hydroxy groups) in the copolymer. The preferred dicarboxylic acids are those containing from 5 to 13 carbon atoms per molecule. The most desirable acids are adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanoic acid and brassylic acid.

The powder coating compositions advantageously contain a flow control agent as a part of the powder coating mixture. The flow control agent is a polymer having a

molecular weight (\bar{M}_n) of at least 1000 and advantageously comprises from 0.05 to 4.0 weight percent of the mixture. The flow control agent suitably has a glass transition temperature at least 20°C. below the glass transition temperature of the mixture's copolymer.

One group of suitable flow control agents are acrylic polymers. Preferred acrylic polymers which may be used for the flow control agent are polyacrylate, polybutyl acrylate, poly (2-ethylhexyl acrylate), polyacryl methacrylate and poly-isodecyl methacrylate.

The flow control agent may also be a fluorinated polymer having a surface tension, at the baking temperature of the powder, lower than that of the copolymer utilized in the mixture. Preferred such flow control agents are esters of polyethyleneglycol or polypropyleneglycol and fluorinated fatty acids. For example, an ester of polyethyleneglycol of molecular weight of over 2500 and perfluorooctanoic acid is a useful flow control agent. Polymeric siloxanes of molecular weight of over 1000, advantageously 1000 to 20,000, may also be useful as flow control agents, e.g. polydimethylsiloxane or polymethylphenylsiloxane.

A coating composition formed in accordance with the teachings of this invention may include a small weight percent of a catalyst in order to increase the crosslinking rate of the powder coating composition at the baking temperature thereof. Baking temperatures will ordinarily be in the range of 130° to 200°C. and the catalyst should produce a gel time for the powder coating composition at the baking temperature to be used which is at least 1 minute but no greater than 40 minutes. This gel time is preferably from 1 to 12 minutes and most preferably from 2 to 8 minutes at the baking temperature.

Catalysts which are suitable for use in the powder coating compositions include quaternary tetraalkylammonium salts, imidazole type catalyst, tertiary amines and metal salts of organic carboxylic acids. The quaternary ammonium salt catalysts include the following: tetrabutylammonium chloride (bromide or iodide), trimethylbenzylammonium chloride, dodecyltrimethyl (2-phenoxyethyl) ammonium bromide and diethyl (2-hydroxy ethyl) methylammonium bromide. Suitable catalysts of the imidazole type include: 2-methyl-4-ethylimidazole, 2-methylimidazole, imidazole, 2-[(N-benzyl-anilino)methyl]-2-imidazoline phosphate and 2-benzyl-2-imidazoline hydrochloride. Suitable tertiary amine catalysts for the powder coating compositions of this invention include: triethylenediamine, N,N-diethylcyclohexylamine and N-methylmorpholine. The metal salts of organic carboxylic acids which are catalysts for the powder coatings of this invention include, for example stannous octoate, zinc naphthenate, cobalt naphthenate, zinc octoate, stannous 2-ethylhexoate, phenylmercuric propionate, lead neodecanoate, dibutyltin dilaurate and lithium benzoate.

The catalyst used in an individual powder coating composition is generally solid at room temperature and suitably has a melting point of from 50°C. to 200°C.

Conventional non-metallic and metallic pigments can be used with the powder coating compositions and are conventionally employed in an amount such as to constitute from 6 to 35 weight percent of the total mixture depending on the pigment selected and the gloss required for the baked coating.

Since individual powder coating compositions of this invention can be applied to an article to be painted by electrostatic methods, it may be desirable to include a small weight percentage of an antistatic agent in such compositions. In particular, the antistatic agent is included in an amount of from 0.05 weight percent of the total powder composition. Suitable antistatic agents include, for example, quaternary ammonium salts as discussed above and which also serve as catalysts. Other suitable antistatic agents include alkyl poly (ethyleneoxy) phosphate or alkyl poly (ethyleneoxy) phosphates (for example ethyl benzyl poly (ethyleneoxy) phosphate); polyethyleneimine; poly (2-vinyl pyrrolidone); pyridinium chloride; poly (vinyl pyridinium chloride); polyvinyl alcohol or inorganic salts.

A plasticizer may be used in a powder coating composition of this invention if desired. The type of plasticizers used very often include adipates, phosphates, phthalates, sebacates, polyesters derived from adipic acid or azelaic acid, and epoxy or epoxidized

plasticizers. Some of these plasticizers are: dihexyl adipate, diisooctyl adipate, dicyclohexyl adipate, triphenylphosphate, tricresylphosphate, tributylphosphate, dibutylphthalate, dioctylphthalate, butyl octyl phthalate, dioctyl sebacate, butyl benzyl sebacate, dibenzyl sebacate, butanediol-1,4-diglycidyl ether and cellulose acetate butyrate.

In order that the invention may be well

understood the following Examples are given by way of illustration only.

In the examples, the illustrated copolymers vary in molecular weight within the range of from 1500 to 15,000 and the concentration of carboxyl groups of the crosslinking agent per functional group (i.e. epoxy groups and hydroxy groups) in the copolymer is in the range of 0.8 to 1.1.

Example 1

- 20 An epoxy-functional, hydroxy-functional copolymer is prepared from the below listed components in the manner hereinafter described:

Reactants	Amounts, grams	Percent By Weight Of Total Reactants
glycidyl methacrylate	30.0	15
hydroxyethyl methacrylate	10.0	5
25 butyl methacrylate	80.0	40
methyl methacrylate	80.0	40

- The above mentioned monomers are admixed in the proportions above set forth and 11.0 grams of 2,2'-azobis-(2-methylpropionitrile), hereinafter called AIBN, are added to the mixture. The mixture is slowly added to 200 ml of toluene heated to 80°-90°C. which is being stirred vigorously under a nitrogen atmosphere. A condenser is provided at the top of the toluene container to condense the toluene vapors and return the condensed toluene to the container. The monomer mixture is added through a regulating valve and the rate of addition is controlled to maintain a reaction temperature of 90°-110°C. with the rest of the heat supplied from an external heater. After the addition of the monomer mixture is completed (3 hours), 0.8 grams of AIBN dissolved in 10 ml acetone is added over a one half (1/2) hours period and refluxing is continued for two (2) additional hours.
- 30 The resulting powder mixture is roll-milled for 10 minutes at 110°C. The resulting melt is granulated and pulverized to particles of 15-50 microns. The resulting powder obtained in this fashion is a powder coating composition of the invention. The powder is sprayed electrostatically on an earthed steel panel by using an electrostatic powder spray gun operating at 60 KV charging voltage. After deposition of powder, the panel is heated to 175°C. and maintained at that temperature for twenty (20) minutes.
- 35 The glossy coating obtained on the panel has good adhesion to the steel panel and good impact strength. This coating when applied to other substrates such as glass, brass, zinc, aluminum, copper and bronze also exhibits good adhesion. The coatings obtained are not soluble in gasoline, xylene, acetone, methyl ethyl ketone or toluene.

Example 2

- 40 An epoxy-functional, hydroxy-functional copolymer is prepared from the below listed components in the manner hereinafter described:

Reactants	Percent By Weight Of Total Reactants
glycidyl methacrylate	10
hydroxyethyl methacrylate	5
60 butyl methacrylate	45
methyl methacrylate	40

- 45 These monomers are admixed. AIBN in the amount of 6 percent of the total mixture is dissolved in 5.0 ml acetone and added to the monomer mixture. These monomers are reacted using the procedure of Example 1 and an epoxy-functional, hydroxy-functional copolymer is formed. This copolymer has a
- 55 The resultant toluene-polymer solution is diluted with 200 mls. acetone and coagulated in 2 liters of hexane. The white powder is dried in the vacuum oven at 55°C. for 24 hours. Its molecular weight is determined to be $M_w/M_n=6700/3200$ and WPE (molecular weight per epoxide group) is about 1000.
- 60 Forty-seven grams of the prepolymer are ball-milled with 3 grams of a commercially available epichlorohydrin-bisphenol A type diepoxide (melting range 64-76°C., viscosity in poise 0.8-1.7 as a 40% solution in butyl-carbitol, average molecular weight 900 and an average WPE of 450-525), 5.3 grams of azelaic acid, 4.5 grams of titanium dioxide, 4.0 grams of Ferrite yellow (pigment) and 0.4 grams of poly (2-ethylhexyl acrylate) for 3-5 hours. The molecular weight of the poly (2-ethylhexyl acrylate) is determined to be $(\bar{M}_n)=9000$. The fine

- glass transition temperature, hereinafter referred to as Tg. of 53°C. and molecular of $M_w/M_n=5145/2950$.
- One hundred grams of the 47 percent toluene solution of this prepolymer is dispersed with 4.0 grams of azelaic acid, 3.0 grams of the diepoxide used in Example 1, 5.0 grams titanium dioxide, 4.0 grams Ferrite yellow and 0.41 grams of poly (2-ethylhexyl acrylate) of $\bar{M}_n=9000$. The dispersion is accomplished by ball-milling the mixture overnight in a pebble mill. The resulting homogeneous mixture is reduced to 40% total solids with toluene and spray dried at 140°F.
- A homogeneous powder is produced which contains less than 1.3% solvent and is in a form suitable for spraying on substrates mentioned in Example 1.
- After the powder is deposited on steel panels electrostatically as in Example 1, it is cured at 170°C. for 25 minutes. The resulting glossy coating has good adhesion and impact strength. It is not soluble in xylene, toluene, gasoline, methanol and methyl ethyl ketone.

Example 3

An epoxy-functional, hydroxy-functional copolymer is prepared from the following components in the manner hereinafter set forth.

Reactants	Grams	Percent By Weight Of Total Reactants
glycidyl methacrylate	30.0	15
hydroxyethyl methacrylate	6.0	3
butyl methacrylate	84.0	42
methyl methacrylate	80.0	40

AIBN in the amount of 11.0 grams (5.5%) are dissolved in 25 ml acetone and added to the monomer mixture. The monomers are reacted as in Example 1 to produce an epoxy-functional, hydroxy-functional copolymer having molecular weight of $M_w/M_n=6870/3600$ and a Tg. of 54°C.

This copolymer is isolated as in Example 1 and compounded with the same amounts of the same materials as in Example 1 except that 5.5 grams of azelaic acid are used. Compounding is effected with a Brabender Plasticorder extruder 25 110°C. These coatings exhibit good adhesion and impact strength. These coatings exhibit high solvent resistance to toluene, xylene or methyl ethyl ketone for 1 minute.

Example 4

An epoxy-functional, hydroxy-functional copolymer is prepared from the following components in the manner hereinafter set forth:

Reactants	Grams	Percent By Weight Of Total Reactants
glycidyl methacrylate	20.0	10
hydroxyethyl methacrylate	20.0	10
butyl methacrylate	80.0	40
methyl methacrylate	80.0	40

- The above listed monomers are admixed and to this mixture is added 12 grams of AIBN (6%) dissolved in 20 ml of acetone. The monomers are reacted following the procedure of Example 1 and an epoxy-functional hydroxy-functional copolymer is produced having a molecular weight of $M_w/M_n=5670/2970$ and a Tg. of 56°C.
- Isolation and compounding of this prepolymer is carried out following the procedure of Example 1 using the same ingredients, exclusive of the copolymer and azelaic acid, in the same proportions as in Example 1. In this instance, 4.1 grams of azelaic acid are used. Deposition and curing of the coatings is carried out following the procedures of Example 1.
- The procedures of Examples 1—4 are repeated with the single difference that an equimolar amount of glycidyl acrylate is substituted for the glycidyl methacrylate in the copolymer.
- The procedures of Example 1 are repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 20% by weight, hydroxyethyl methacrylate 2% by weight, isobutyl acrylate 25% by weight, alpha-methylstyrene 15% by weight, methacrylonitrile 15% by weight and methyl methacrylate 23% by weight, and (2) 7.9 grams of azelaic acid are used.

Example 5

The procedures of Examples 1—4 are repeated with the single difference that an equimolar amount of glycidyl acrylate is substituted for the glycidyl methacrylate in the copolymer.

Example 6

The procedures of Example 1 are repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 20% by weight, hydroxyethyl methacrylate 2% by weight, isobutyl acrylate 25% by weight, alpha-methylstyrene 15% by weight, methacrylonitrile 15% by weight and methyl methacrylate 23% by weight, and (2) 7.9 grams of azelaic acid are used.

Example 7

5 The procedures of Example 1 are repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 5% by weight, hydroxyethyl methacrylate 10% by weight, acrylonitrile 10% by weight, butyl acrylate 30% by weight and methyl methacrylate 45% by weight.

Example 8

10 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of adipic acid is substituted for the azelaic acid crosslinking agent.

Example 9

15 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of pimelic acid is substituted for the azelaic acid crosslinking agent.

Example 10

20 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of suberic acid is substituted for the azelaic acid crosslinking agent.

Example 11

30 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of sebacic acid is substituted for the azelaic acid crosslinking agent.

Example 12

35 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of undecanoic acid is substituted for the azelaic acid crosslinking agent.

Example 13

40 The procedures of Examples 1—7 are repeated with the single difference that a functionally equivalent amount of brassylic acid is substituted for the azelaic acid crosslinking agent.

Example 14

45 The procedures of Examples 1—7 are repeated with the single difference that in the forming of the copolymer a functional equivalent amount of hydroxyethyl acrylate is substituted for the hydroxyethyl methacrylate.

Example 15

55 The procedures of Examples 1—7 are repeated with the single difference that in the forming of the copolymer a functionally equivalent amount of hydroxypropyl acrylate is substituted for the hydroxyethyl methacrylate.

Example 16

60 The procedures of Examples 1—7 are repeated with the single difference that in the forming of the copolymer a functionally equivalent amount of hydroxypropyl methacrylate is substituted for the hydroxyethyl methacrylate.

65 acrylate is substituted for the hydroxyethyl methacrylate.

Example 17

70 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the powder coating material an equivalent amount of poly (lauryl acrylate)—($M_n=8,000$) is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

Example 18

75 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the powder coating material an equivalent amount of poly (2-ethylhexyl acrylate)— $M_n=11,000$ is substituted for the poly (2-ethylhexyl acrylate) flow control agent ($M_n=9000$).

Example 19

85 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the powder coating material an equivalent amount of poly (butyl acrylate)— $M_n=9,000$ is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

Example 20

90 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the powder coating material an equivalent amount of poly (isodecyl methacrylate)— $M_n=5,000$ is substituted for the poly (2-ethyl acrylate) flow control agent.

Example 21

100 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the coating material an equivalent amount of polyethylene glycol perfluoro-octoate— $M_n=3,400$ is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

Example 22

105 The procedures of Examples 1—7 are repeated with the single difference that in the compounding of the coating material an equivalent amount of poly (methyl siloxane) is substituted for the poly (2-ethylhexyl acrylate) flow control agent.

Example 23

115 The procedures of Examples 1—7 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate), is reduced from 0.42 grams to 0.25 grams.

Example 24

120 The procedures of Examples 1—7 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate), is increased from 0.42 grams to 2.0 grams.

Example 25

The procedures of Examples 1—7 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate), is increased from 0.42 grams to 4.0 grams.

Example 26

The procedures of Examples 1—7 are repeated with the single difference that the copolymer is formed from the following monomers:

Reactants	Percent By Weight Of Total Reactants
glycidyl methacrylate	15
15 hydroxyethyl methacrylate	6
vinyl chloride	22
butyl methacrylate	17
methyl methacrylate	40

Example 27

The procedure of Example 1 is repeated except for the the differences that (1) the copolymer is formed from glycidyl methacrylate 20% by weight, hydroxyethyl methacrylate 2% by weight, butyl acrylate 20% by weight, and methyl methacrylate 58% by weight, (2) 7% by weight of the reaction initiator is employed in reacting the monomer mixture to form the copolymer, and (3) 8.0 parts by weight of azelaic acid are compounded with 47.0 parts by weight of the copolymer and the other components of the coating material in Example 1, the latter being employed in the same amounts as in Example 1. The molecular weight of the copolymer (\bar{M}_n) is about 1500.

Example 28

The procedure of example 1 is repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 8% by weight; hydroxy ethyl methacrylate 5% by weight, butyl acrylate 22% by weight, methyl methacrylate 60% by weight and styrene 6% by weight, (2) 0.8% by weight of the reaction initiator is employed in reacting the monomer mixture to form the polymer, and (3) 3.2 grams of azelaic acid are compounded with 50 grams of the copolymer and the other components of the coating material in Example 1, the latter being employed in the same amount, as in Example 1. Deposition and curing of the coatings is carried out following the procedure of Example 1. The molecular weight of this copolymer (\bar{M}_n) is about 15,000.

The coatings heretofore exemplified when sprayed on a variety of wood, metal and glass substrates and heat cured thereon provide coatings which demonstrate good

adhesion to the substrate and good organic solvent resistance.

In our copending Application No. 43749/72 (Serial No. 1,410,662) we describe a moulding powder comprising (a) an epoxy-group containing acrylic copolymer derived from glycidyl methacrylate, methyl methacrylate and, optionally, acrylonitrile and/or methacrylonitrile; and (b) a dicarboxylic acid crosslinking agent therefor.

WHAT WE CLAIM IS:—

1. A powder coating composition comprising a mixture of:—

- (A) A copolymer derived from 5 to 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid, from 2 to 10 percent by weight of a C_6-C_7 hydroxyalkyl acrylate or methacrylate and from 70 to 93 percent by weight of one or more other monoethylenically unsaturated monomers, and having a glass transition temperature of from 40 to 90°C and a number average molecular weight of from 1500 to 15,000, and
- (B) a saturated, straight chain, aliphatic dicarboxylic acid containing from 4 to 20 carbon atoms present in an amount to provide from 0.8 to 1.1 carboxyl groups for each functional group (i.e. epoxy or hydroxy group) in the copolymer.

2. A composition as claimed in Claim 1 in which the copolymer is derived from 8 to 15 percent by weight of the said glycidyl ester.

3. A composition as claimed in Claim 1 or Claim 2 in which the said glycidyl ester is glycidyl acrylate or glycidyl methacrylate.

4. A composition as claimed in any one of the preceding claims in which the said hydroxy acrylate is an ester of a C_2-C_3 dihydric alcohol and acrylic or methacrylic acid.

5. A composition as claimed in any one of the preceding claims in which the other monoethylenically unsaturated monomers consist essentially of esters of acrylic or methacrylic acid and a C_1-C_8 monohydric alcohol.

6. A composition as claimed in any one of the preceding claims in which the copolymer has a glass transition temperature of from 50 to 80°C.

7. A composition as claimed in any one of the preceding claims in which the copolymer has a molecular weight of from 2,500 to 6,000.

8. A composition as claimed in any one of the preceding claims in which the dicarboxylic acid contains from 5 to 13 carbon atoms.

9. A composition as claimed in any one

Example 25

The procedures of Examples 1-7 are repeated with the single difference that the flow control agent, poly (2-ethylhexyl acrylate), is increased from 0.42 grams to 4.0 grams.

Example 26

The procedures of Examples 1-7 are repeated with the single difference that the copolymer is formed from the following monomers:

Reactants	Percent By Weight Of Total Reactants
glycidyl methacrylate	15
15 hydroxyethyl methacrylate	6
vinyl chloride	22
butyl methacrylate	17
methyl methacrylate	40

Example 27

The procedure of Example 1 is repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 20% by weight, hydroxyethyl methacrylate 2% by weight, butyl acrylate 20% by weight, and methyl methacrylate 58% by weight, (2) 7% by weight of the reaction initiator is employed in reacting the monomer mixture to form the copolymer, and (3) 8.0 parts by weight of azelaic acid are compounded with 47.0 parts by weight of the copolymer and the other components of the coating material in Example 1, the latter being employed in the same amounts as in Example 1. The molecular weight of the copolymer (\bar{M}_n) is about 1500.

Example 28

The procedure of example 1 is repeated except for the differences that (1) the copolymer is formed from glycidyl methacrylate 8% by weight; hydroxy ethyl methacrylate 5% by weight, butyl acrylate 22% by weight, methyl methacrylate 60% by weight and styrene 6% by weight, (2) 0.8% by weight of the reaction initiator is employed in reacting the monomer mixture to form the polymer, and (3) 3.2 grams of azelaic acid are compounded with 50 grams of the copolymer and the other components of the coating material in Example 1, the latter being employed in the same amount, as in Example 1. Deposition and curing of the coatings is carried out following the procedure of Example 1. The molecular weight of this copolymer (\bar{M}_n) is about 15,000.

The coatings heretofore exemplified when sprayed on a variety of wood, metal and glass substrates and heat cured thereon provide coatings which demonstrate good

adhesion to the substrate and good organic solvent resistance.

In our copending Application No. 43749/72 (Serial No. 1,410,662) we describe a moulding powder comprising (a) an epoxy-group containing acrylic copolymer derived from glycidyl methacrylate, methyl methacrylate and, optionally, acrylonitrile and/or methacrylonitrile; and (b) a dicarboxylic acid crosslinking agent therefor.

WHAT WE CLAIM IS:—

1. A powder coating composition comprising a mixture of:—

- (A) A copolymer derived from 5 to 20 weight percent of a glycidyl ester of a monoethylenically unsaturated acid, from 2 to 10 percent by weight of a C_6-C_7 hydroxyalkyl acrylate or methacrylate and from 70 to 93 percent by weight of one or more other monoethylenically unsaturated monomers, and having a glass transition temperature of from 40 to 90°C and a number average molecular weight of from 1500 to 15,000, and
- (B) a saturated, straight chain, aliphatic dicarboxylic acid containing from 4 to 20 carbon atoms present in an amount to provide from 0.8 to 1.1 carboxyl groups for each functional group (i.e. epoxy or hydroxy group) in the copolymer.

2. A composition as claimed in Claim 1 in which the copolymer is derived from 8 to 15 percent by weight of the said glycidyl ester.

3. A composition as claimed in Claim 1 or Claim 2 in which the said glycidyl ester is glycidyl acrylate or glycidyl methacrylate.

4. A composition as claimed in any one of the preceding claims in which the said hydroxy acrylate is an ester of a C_6-C_7 dihydric alcohol and acrylic or methacrylic acid.

5. A composition as claimed in any one of the preceding claims in which the other monoethylenically unsaturated monomers consist essentially of esters of acrylic or methacrylic acid and a C_1-C_8 monohydric alcohol.

6. A composition as claimed in any one of the preceding claims in which the copolymer has a glass transition temperature of from 50 to 80°C.

7. A composition as claimed in any one of the preceding claims in which the copolymer has a molecular weight of from 2,500 to 6,000.

8. A composition as claimed in any one of the preceding claims in which the dicarboxylic acid contains from 5 to 13 carbon atoms.

9. A composition as claimed in any one